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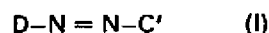
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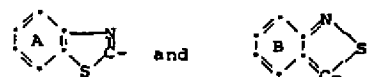
(58) Field of search
C4P

(54) Disperse and acid azo dyes having 1,2-dihydroquinoline couplers

(57) New dyes of formula (I) give blue to green shades on polyamide fibres:



wherein C' is an optionally substituted 1,2-dihydroquinoline coupler, and D is selected from:



wherein rings A and B are optionally substituted.

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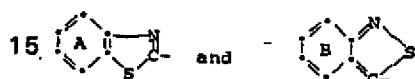
SPECIFICATION

Disperse and acid azo dyes having 1,2-dihydroquinoline couplers

- 5 This invention concerns disperse and acid dyes particularly suited for the dyeing of polyamide fibres, and having the general formula 5



- wherein D is 2-benzothiazolyl or 3-benzisothiazolyl, unsubstituted or substituted with 1-3 substituents such as acyl, acylamido, alkyl, carboalkoxy, alkyl-SO₃M acylamido, halogen, and
 10 cyano and C¹ is a 1,2-dihydroquinoline coupler which is unsubstituted or substituted. 10
 More particularly the dyes correspond to the formula above wherein D is selected from

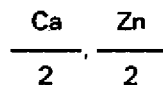


- wherein rings A and B may have 1-3 substituents independently selected from alkyl, cyclohexyl, aryl, alkoxy, thiocyno, alkylthio, arylthio, cyano, nitro, CONH₂, CONHalkyl, CON(alkyl)₂, alkoxycarbonyl, alkanoyl, aroyl, alkanoyloxy, alkylsulfonyl, SO₂NH₂, SO₂NHalkyl, SO₂N(alkyl)₂, alkyl-SO₃M, alkylsulfonamido, acylamido, halogen, trifluoromethyl, SO₃-aryl, SO₃-alkyl, and alkenyl of 2-8 carbons; and C¹ is represented by the formula 20

- 25  25

- 30 R₁ is H, alkyl, aryl or cyclohexyl;
 R₂ and R₃ are each independently selected from H and alkyl;
 R₄ is H, alkyl, or alkyl-SO₃M; and
 R₅ is selected from H, alkyl, alkoxy, alkenyl of 2-8 carbons, halogen, acylamido, alkylthio and
 35 formamido, wherein the alkyl moieties thereof may be substituted with 1-3 substituents 35
 independently selected from hydroxy, halogen, cyano, alkoxy, alkylthio, alkanoyl, alkanoyloxy, and alkoxycarbonyl;

- wherein all of the alkyl, alkylene, alkenyl and cyclic moieties in the defined substituents for rings A and B, and for R₁, may themselves be substituted with 1-3 substituents different from
 40 the said moiety and independently selected from hydroxy, alkoxy, aryl, aryloxy, cyclohexyl, cyclohexoxy, furyl (C₄H₃O), aroyloxy, alkoxycarbonyl, alkanoyloxy, SO₂NH₂, SO₂NHaryl, SO₂N-alkyl, SO₂N(alkyl)₂, alkyl-SO₃M, NHCOOalkyl, NHCONHalkyl, acylamido, alkylsulfonamido, succinimido (C₄H₄O₂N), glutarimido (C₅H₆O₂N), phthalimido (C₆H₄O₂N), 1-(2-pyrrolidono) (C₄H₆ON), cyano, CONH₂, CONHalkyl, CON(alkyl)₂, alkoxyalkoxy, alkylthio, halogen, arylthio, 45 alkylsulfonyl and arylsulfonyl; and wherein each M is selected from H, Na, K, NH₄. 45



- 50 and the colorless cations of salts of primary, secondary and tertiary aliphatic and aryl amines. 50
 Preferred of the present dyes are where D is selected from

- 55  and 55

- 60 wherein rings A and B are unsubstituted or substituted with 1-3 substituents independently 60
 selected from cyano, alkylsulfonyl, SO₂NH₂, -NO₂, alkyl-SO₃M, SO₂NHalkyl, SO₂N(alkyl)₂, and halogen.

- The various alkyl or alkylene moieties in, for example, alkoxy, alkanoyl, and alkoxyalkoxy, within the above definitions of R₁-R₅ and the A and B ring substituents, have 1-6 carbons, and
 65 they and the alkenyl groups are straight or branched chain. 65

The dyes of this invention impart blue to green shades on fibers, particularly polyamides, exhibiting improvements in one or more properties such as fastness to light, ozone, perspiration, oxides of nitrogen, washing, sublimation or crocking, and in leveling, transfer, pH stability, exhaustion, build and non-red flaring, and the acid dyes are surprisingly bathochromic.

- 5 The diazo components useful in this invention are prepared according to procedures well known to the art. The present dyes may be applied to polyamide fibers by conventional dyeing procedures, e.g., dispersed in a lignin sulfonate and dyed at 98°C. on nylon fabric for one hour from an aqueous bath. The following examples illustrate procedures which are generally applicable for preparation of the present couplers and dyes.

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EXAMPLE 1

(a)—*Procedure For the Preparation of 1,2-Dihydro-2,2,4,7-Tetramethylquinoline*

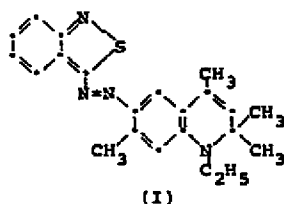
Meta-toluidine (535 g.) and iodine (6 g.) are charged to a 2 liter, 3 neck, round bottom flask. The reaction is heated to 155°C. and about 3,500 g. of acetone is added at 155–160°C.

- 15 beneath the surface over a 12 hour period. A mixture of acetone and water distills off during the addition. The reaction mixture is heated one-half hour at 160°C. and then distilled to about 690 g. of 1,2-dihydro-2,2,4,7-tetramethylquinoline boiling at 107–111°C. at 0.55 mm., a 74% yield. This product is then ethylated with triethylphosphate in the presence of ethyl iodide in known manner.

- 20 (b)—*Diazotization and Coupling*

Sodium nitrite (0.72 g., 0.0104 mole) was added to sulphuric acid (5.0 cc.) and the solution warmed to 70°C., for 5 minutes. 1–5 Acid, a propionic-acetic acid mixture (1:5 molar ratio) (10.0 cc.) was added below 20°C. The mixture was cooled to 0°C. and 3-amino-2,1-benzisothiazole (1.50 g., 0.01 mole) was added, followed by a further 10.0 cc. of 1–5 acid. The mixture was stirred at 0–5°C. for two hours and then added to the coupler of Example 1 (10.75 g., 0.05 mole) in 50% aqueous ethanol (54.0 cc.) containing sodium acetate (2.05 g.), at <5°C. After stirring at 0–5°C. for one hour the dye was warmed to room temperature and precipitated by adding to cold water. The product was filtered and washed well with water to yield 2.61 g. (69.5%) of the final dye product, I.

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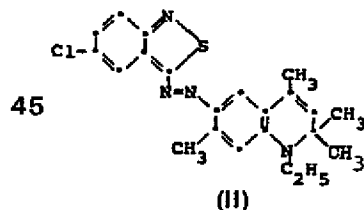


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(I)

EXAMPLE 2

- 40 By application of the above Example 1(b) procedure, Dye II was prepared in 63% yield.



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(II)

- 50 The preparation of the sulfonated 1,2-dihydroquinoline is given in German Offen. 3,005,874 (C.A. 94, 15593K, 1981) and comprises sulfonating the 4-alkyl-1,2-dihydroquinoline with H₂SO₄, ClSO₃H, and/or SO₃ and converting, if desired, the acid group to its salt in known manner.

The acid dyes of the invention may be applied to polyamide fiber by the following method:

- 55 The test dye, as a mixture with a sulphate such as ammonium sulfate, is pasted with boiling water and then made up to a known volume with water to give a weight ratio of water to dye of 30:1. Four percent on weight of fiber (owf) of a lignin sulphonate leveling agent is added, followed by ammonium acetate (about 3.0% owf) to adjust the pH to 6. The initial dyeing temperature is 40°C. which is raised to the final dyeing temperature of 98°C. over 30 minutes. The dye bath is held at 98°C. for 60 minutes, then cooled, and the test fabric given a warm water rinse and air drying.

EXAMPLE 3

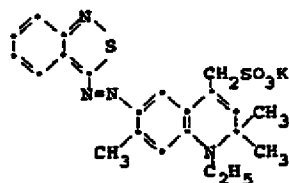
- 65 Sodium nitrite (0.72 g., 0.0104 mole) was added to sulphuric acid (5.00 cc.) and the solution warmed to 70°C., for 5 minutes. Ten cc. of 1–5 acid was added, at less than 20°C.

The mixture was cooled to 0°C. and 3-amino,2,1-benzisothiazole (1.50 g., 0.01 mole) was added, followed by a further 10.00 cc. of 1:5 acid. The mixture was stirred at 0-5°C. for two hours then added to the potassium salt of 1-ethyl-2,2,7-tri-methyl-1,2-dihydroquinolin-4-yl-methyl sulfonic acid (3.33 g., 0.01 mole) in 11 cc. of water at <5°C. This yielded 3.36 g.

5 (68.0%) of the final dye product (III).

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(III)

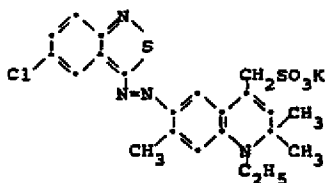
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15 EXAMPLE 4

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By application of the above procedure, in Example 4, Dye (IV) was prepared in 3.44 g. (65.0%) yield.

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(IV)

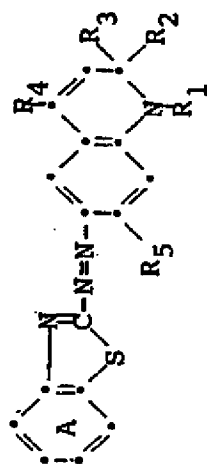
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The following tables further show specific dyes of the present invention which are prepared as above.

TABLE 1



Substituents on Ring A	R ₅	R ₂	R ₃	R ₄	R ₁
None	H	H	H	H	H
None	H	H	CH ₃	CH ₃	C ₂ H ₅
5,6-di-CH ₂ CH ₂ OH	CH ₃	CH ₃	CH ₃	CH ₃	C ₃ H _{7-n}
6-CH ₂ OC ₆ H ₅	CH ₂ CH ₂ OH	CH ₃	CH ₃	CH ₃	C ₄ H _{9-n}
6-CH ₂ CH ₂ OC ₆ H ₁₁	CH ₂ Cl	H	CH(CH ₃) ₂	CH ₃	CH ₂ CH ₂ SO ₂ NHC ₆ H ₅
5-NO ₂	OCH ₂ Cl	H	CH ₃	CH ₃	CH ₂ CH ₂ OC ₆ H ₅
6-CH ₂ COOCH ₃	OCH ₃	H	CH ₃	CH ₂ SO ₃ K	CH ₃
5-CH ₂ (C ₄ H ₃ O)	OCH ₃	H	CH ₃	CH ₂ CH ₂ SO ₃ Na	C ₆ H ₅
6-CH ₂ CH ₂ OOCC ₆ H ₅	CH ₂ CH ₂ CN	H	CH ₃	H	C ₆ H ₁₁
6-CH ₂ OOCC ₃	CH ₂ SO ₃ Na	H	CH ₃	CH ₃	C ₂ H ₄ OC ₆ H ₁₁
6-SCH ₂ SO ₂ NH ₂	Cl	H	CH ₃	CH ₃	CH ₂ CH ₂ SO ₂ NH ₂

6-CH ₃	H	CH ₃	CH ₂ SO ₃ NH(Et) ₃	CH ₂ CH ₂ OH
6-CONHCH ₃	OCH ₃	C ₂ H ₅	C ₂ H ₅	CH ₂ CH ₂ SO ₂ N(C ₂ H ₅) ₂
6-CON(C ₂ H ₅) ₂	NHCHO	CH ₃	CH ₃	CH ₂ CH ₂ OC ₂ H ₅
6-CH ₂ SO ₂ NHCH ₃	NHCOCH ₂ OCCH ₃	CH ₃	CH ₃	CH ₂ CN
6-C ₆ H ₅	NHCOCH ₂ CH ₃	C ₃ H ₇ -n	H	CH ₂ CONH ₂
6-CH ₃	NHCOCH ₂ Cl	CH ₃	H	CH ₂ CONHCH ₃
5-CH ₂ NHCOOCH ₃	NHCOC ₆ H ₅	CH ₃	H	CH ₂ CON(C ₂ H ₅) ₂
6-SCN	NHCOC ₂ H ₅	C ₄ H ₉ -n	H	CH ₂ NHCOCH ₃
6-CH ₂ NHCONHCH ₃	NHCOC ₆ H ₁₁	CH ₃	H	CH ₂ NHCOOCH ₃
6-OCH ₃	H	CH ₃	H	CH ₂ OOCCH ₃
6-Br	CH ₂ SCH ₃	CH ₃	H	CH(C ₄ H ₉ ON)
6-CF ₃	CH ₂ CH=CH ₂	H	H	CH ₂ CH ₂ COOCH ₃
6-OCH ₂ CH ₃	Br	CH ₃	CH ₂ SO ₃ (Ca/2)	CH ₂ CH ₂ COOCH ₃
6-SCH ₃	I	CH ₃	CH ₂ SO ₃ (Zn/2)	H
6-SCN	F	CH ₃	CH ₂ SO ₃ NH ₄	C ₂ H ₄ SC ₂ H ₅
6-SO ₂ NH ₂	SCH ₃	CH ₃	CH ₃	C ₃ H ₇ -n
6-SO ₂ NHC ₄ H ₉ -n	CH ₂ OOCCH ₃	CH ₃	CH ₃	C ₄ H ₉ -n

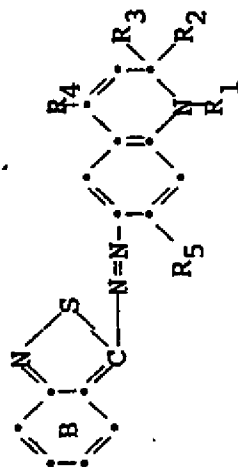
6-SO ₂ N(CH ₃) ₂	OCH ₃	H	CH ₃	CH ₃	C ₂ H ₄ C ₆ H ₅
6-SO ₃ C ₆ H ₅	CH ₃	H	CH ₃	CH ₂ NH(CH ₂ CH ₂ OH) ₃	C ₂ H ₄ C ₆ H ₁₁
6-CN	H	H	H	H	CH ₂ Cl
6-CONH ₂	CH ₂ CH ₂ COOCH ₃	H	CH ₃	CH ₃	C ₆ H ₄ -p-OCH ₃
4-COOCH ₃	CH ₂ CH(OH)CH ₂ OH	H	CH ₃	CH ₃	C ₆ H ₁₀ -p-OH
6-COCH ₃	CF ₃	H	CH ₃	CH ₃	C ₂ H ₅
6-COC ₆ H ₅	CF ₃	H	CH ₃	CH ₃	CH ₂ CH ₂ SC ₆ H ₅
6-Cl	H	C ₂ H ₅	C ₂ H ₅	CH ₃	CH ₂ CH ₂ SO ₂ CH ₃
5,6-di-Cl	H	C ₂ H ₅	C ₂ H ₅	CH ₂ SO ₃ K	CH ₂ CH ₂ SO ₂ C ₆ H ₅
4-Br	CH ₂ CH(Cl)CH ₂ Cl	C ₂ H ₅	C ₂ H ₅	CH ₂ SO ₃ H	CH ₂ CH ₂ OC ₂ H ₄ OC ₂ H ₅
4-CF ₃	CH ₂ CH(OCH ₃)CH ₂ OCH ₃	CH ₃	CH ₃	CH ₃	CH ₂ (C ₈ H ₄ O ₂ N)
6-NHCOCH ₃	CH ₃	CH ₃	CH ₃	CH ₃	CH ₂ CONH ₂
6-SO ₂ CH ₃	CH ₃	CH ₃	CH ₃	CH ₃	CH ₂ (C ₄ H ₄ O ₂ N)
6-CH ₂ SO ₂ NHC ₂ H ₅	CH ₃	CH ₃	CH ₃	CH ₃	CH ₂ CON(C ₂ H ₅) ₂
6-CH ₂ SO ₂ N(C ₂ H ₅) ₂	CH ₃	CH ₃	CH ₃	CH ₃	CH ₂ NHCONHCH ₃
6-SO ₂ NHC ₂ H ₅	H	CH ₃	CH ₃	CH ₃	CH ₂ NHSO ₂ CH ₃
6-CH ₂ CH ₂ NHCOCH ₂ Cl	H	CH ₃	CH ₃	CH ₃	CH ₂ OOCCH ₃

6-CH ₂ NHSO ₂ CH ₃	CH ₃	CH ₃	CH ₃	CH ₃	CH ₂ (C ₄ H ₃ O)
6-CH ₂ CH ₂ CH ₂ (C ₄ H ₆ ON)	CH ₂ CH ₂ OH	CH ₃	CH ₃	H	CH ₂ CH ₂ COOCH ₃
None	CH ₂ Cl	CH ₃	CH ₃	H	CH ₂ CH ₂ OOC ₆ H ₅
6-CH ₂ CH ₂ CN	OCH ₂ Cl	CH ₃	CH ₃	C ₃ H ₇ -n	H
6-NHCOCH ₂ CN	OCH ₃	CH ₃	CH ₃	C ₃ H ₇ -n	C ₂ H ₅
6-CH ₂ (C ₄ H ₄ O ₂ N)	OCH ₃	CH ₃	CH ₃	C ₂ H ₅	C ₃ H ₇ -n
6-CH ₂ (C ₅ H ₆ O ₂ N)	CH ₂ CH ₂ CN	CH ₃	CH ₃	C ₂ H ₅	C ₄ H ₉ -n
6-CH ₂ CH ₂ (C ₈ H ₄ O ₂ N)	Cl	CH ₃	CH ₃	C ₂ H ₅	C ₂ H ₅
5-CH ₂ CONH ₂	Cl	CH ₃	CH ₃	CH ₃	C ₂ H ₅
6-CH ₂ CONHCH ₃	H	CH ₃	CH ₃	CH ₃	CH ₃
6-CH ₂ CH ₂ OCH ₂ CH ₂ OC ₂ H ₅	OCH ₃	CH ₃	CH ₃	CH ₃	C ₆ H ₅
6-COOCH ₂ CH ₂ OCH ₃	NHCHO	CH ₃	CH ₃	CH ₃	C ₆ H ₁₁
6-CH ₂ CH ₂ SC ₂ H ₃	NHCOCH ₂ OCH ₃	CH ₃	CH ₃	CH ₃	C ₂ H ₅
6-CH ₂ CH ₂ CH ₂ Cl	NHCOCH ₂ CH ₃	H	H	H	CH ₂ CH ₂ OH
6-CH ₂ SC ₆ H ₅	NHCOCH ₂ Cl	H	CH ₃	CH ₃	CH ₂ CH ₂ OH
5-CH ₂ SO ₂ CH ₃	NHCOC ₆ H ₅	CH ₃	CH ₃	CH ₃	CH ₂ CH ₂ OH
6-CH ₂ SO ₂ C ₆ H ₅	NHCOC ₂ H ₅	CH ₃	CH ₃	CH ₃	CH ₂ CH ₂ OC ₂ H ₅

6-CH ₂ CH(OH)CH ₂ OH	NHCOC ₆ H ₁₁	H	CH(CH ₃) ₂	CH ₃	CH ₂ CN
6-CH ₂ CH(OH)CH=CH ₂	H	H	CH ₃	CH ₃	CH ₂ CONH ₂
4-C ₆ H ₄ -p-OH	CH ₂ SCH ₃	H	CH ₃	H	CH ₂ CONHCH ₃
5-C ₆ H ₄ -p-C ₂ H ₅	CH ₂ CH=CH ₂	H	CH ₃	H	CH ₂ CON(C ₂ H ₅) ₂
6-C ₆ H ₄ -p-OC ₆ H ₅	Br	H	CH ₃	H	CH ₂ NHCOCH ₃
6-C ₆ H ₄ -p-C ₆ H ₁₁	I	H	CH ₃	CH ₃	CH ₂ NHCOOCH ₃
6-C ₆ H ₄ -p-(C ₄ H ₃ O)	F	H	CH ₃	CH ₃	CH ₂ OOCCH ₃
6-C ₆ H ₄ -p-OCC ₆ H ₅	SCH ₃	H	CH ₃	CH ₃	CH ₂ (C ₄ H ₆ ON)
6-C ₆ H ₄ -o-COOCH ₃	CH ₂ OOCCH ₃	C ₂ H ₅	C ₂ H ₅	C ₂ H ₅	CH ₂ CH ₂ COCH ₃
6-C ₆ H ₄ -m-SO ₂ NH ₂	OCH ₃	CH ₃	CH ₃	CH ₃	CH ₂ CH ₂ COOCH ₃
6-C ₆ H ₄ -p-CONH ₂	CH ₃	CH ₃	CH ₃	CH ₃	H
6-C ₆ H ₄ -p-NHCONHCH ₃	H	C ₃ H ₇ -n	C ₃ H ₇ -n	H	C ₂ H ₅
5-C ₆ H ₄ -m-(C ₈ H ₄ O ₂ N)	CH ₂ CH ₂ COOCH ₃	CH ₃	CH ₃	H	C ₃ H ₇ -n
5-C ₆ H ₃ -o,p-di-CN	CH ₂ CH(OH)CH ₂ OH	CH ₃	CH ₃	H	C ₄ H ₉ -n
6-C ₆ H ₂ -o,m,p-tri-Cl	CF ₃	C ₄ H ₉ -n	C ₄ H ₉ -n	H	C ₂ H ₅
6-C ₆ H ₄ -p-OCH ₂ OCH ₃	CF ₃	CH ₃	CH ₃	H	C ₂ H ₅
6-C ₆ H ₄ -p-SC ₆ H ₅	H	CH ₃	CH ₃	H	CH ₃

5-C ₆ H ₄ -p-SO ₂ CH ₃	H	H	CH ₃	H	C ₆ H ₅
5-C ₆ H ₄ -p-SO ₂ C ₆ H ₅	CH ₂ CH(Cl)CH ₂ Cl	H	H	H	C ₆ H ₁₁
5-C ₆ H ₁₀ -p-Cl	CH ₂ CH(OCH ₃)CH ₂ OCH ₃	H	CH ₃	CH ₃	C ₂ H ₅
6-C ₆ H ₉ -o,p-di-OH	CH ₃	H	CH ₃	CH ₃	CH ₂ CH ₂ OH
6-C ₆ H ₁₀ -p-CH ₃	CH ₃	H	CH ₃	CH ₃	CH ₂ CH ₂ OH
6-C ₆ H ₁₀ -p-OC ₂ H ₅	CH ₃	H	CH ₃	CH ₃	CH ₂ CH ₂ OH
6-CH ₂ CH ₂ SO ₂ NHC ₆ H ₅	CH ₃	H	CH ₃	CH ₃	CH ₂ CH ₂ OC ₂ H ₅
6-C ₆ H ₄ -p-SO ₂ NHC ₆ H ₅	H	H	CH ₃	CH ₃	CH ₂ CN
6-CH ₂ CH ₂ OCH ₂ C ₆ H ₅	H	H	CH ₃	CH ₃	CH ₂ CONH ₂
5-C ₆ H ₁₁	H	H	CH ₃	CH ₃	C ₆ H ₄ -p-(C ₄ H ₄ O ₂ N)
5-SC ₆ H ₅	H	H	CH ₃	CH ₃	C ₆ H ₁₀ -p-OCH ₃
6-OOCCH ₃	CH ₃	CH ₃	CH ₃	CH ₃	C ₆ H ₄ -p-Cl
6-SO ₃ -CH ₃	CH ₃	CH ₃	CH ₃	CH ₃	CH ₂ (C ₅ H ₆ O ₂ N)
6-SO ₃ K	CH ₃	CH ₃	CH ₃	CH ₃	C ₂ H ₅
6-SO ₃ NH(Et) ₃	CH ₃	CH ₃	CH ₃	CH ₃	CH ₂ CH ₂ OH

TABLE 2



Substituents on Ring B	R ₅	R ₂	R ₃	R ₄	R ₁
None	H	H	H	H	H
None	H	H	CH ₃	CH ₃	C ₂ H ₅
5,6-di-CH ₂ CH ₂ OH	CH ₃	CH ₃	CH ₃	CH ₃	C ₃ H ₇ -n
5-CH ₂ OC ₆ H ₅	CH ₂ CH ₂ OH	CH ₃	CH ₃	CH ₃	C ₄ H ₉ -n
6-CH ₂ CH ₂ OC ₆ H ₁₁	CH ₂ Cl	H	CH(CH ₃) ₂	CH ₃	C ₂ H ₅
6-NO ₂	OCH ₂ Cl	H	CH ₃	CH ₃	C ₂ H ₅
6-CH ₂ COOCH ₃	OCH ₃	H	CH ₃	CH ₂ SO ₃ K	C ₆ H ₃ -o,p-di-Cl
5-CH ₂ (C ₄ H ₃ O)	OCH ₃	H	CH ₃	CH ₂ CH ₂ SO ₃ Na	C ₆ H ₄ -p-CONH ₂
5-CH ₂ CH ₂ OOC ₆ H ₅	CH ₂ CH ₂ CN	H	CH ₃	H	C ₆ H ₁₀ -p-OH
5-CH ₂ OOCCH ₃	CH ₂ SO ₃ Na	H	CH ₃	CH ₃	C ₆ H ₄ -m-OCH ₃
5-SCH ₂ SO ₂ NH ₂	Cl	H	CH ₃	CH ₂ SO ₃ NH(Et) ₃	CH ₂ CH ₂ OH

5-CH ₃	H		CH ₃	CH ₃	C ₆ H ₄ -p-SCH ₃
5-CONHCH ₃	OCH ₃		C ₂ H ₅	C ₂ H ₅	C ₆ H ₄ -p-SO ₂ CH ₃
5-CON(C ₂ H ₅) ₂	NHCHO		CH ₃	CH ₃	CH ₂ CH ₂ OC ₂ H ₅
5-CH ₂ SO ₂ NHCH ₃	NHCOCH ₂ OCCH ₃		CH ₃	CH ₃	C ₆ H ₄ -p-SO ₂ NHCH ₃
5-C ₆ H ₅	NHCOCH ₂ CH ₃		C ₃ H ₇ -n	C ₃ H ₇ -n	CH ₂ CONH ₂
6-CH ₃	NHCOCH ₂ Cl		CH ₃	CH ₃	C ₆ H ₄ -m-SO ₂ N(C ₂ H ₅) ₂
5-CH ₂ NHCOOCH ₃	NHCOC ₆ H ₅		CH ₃	CH ₃	CH ₂ CON(C ₂ H ₅) ₂
6-SCN	NHCOC ₂ H ₅		C ₄ H ₉ -n	C ₄ H ₉ -n	CH ₂ NHCOCH ₃
6-CH ₂ NHCONHCH ₃	NHCOC ₆ H ₁₁		CH ₃	CH ₂ SO ₃ (Ca/2)	CH ₂ NHCOOCH ₃
6-OCH ₃	H		CH ₃	CH ₂ SO ₃ (Zn/2)	CH ₂ OOCCH ₃
5-Br	CH ₂ SCCH ₃		CH ₃	CH ₂ SO ₃ NH ₄	CH(C ₄ H ₆ ON)
5-CF ₃	CH ₂ CH=CH ₂		H	H	CH ₂ CH ₂ COOCH ₃
5-OCH ₂ CH ₃	Br		CH ₃	CH ₃	CH ₂ CH ₂ COOCH ₃
5-SCH ₃	I		CH ₃	CH ₃	H
5-SCN	F		CH ₃	CH ₃	C ₂ H ₅
5-SO ₂ NH ₂	SCH ₃		CH ₃	CH ₂ NH(CH ₂ CH ₂ OH) ₃	C ₃ H ₇ -n
5-SO ₂ NHC ₄ H ₉ -n	CH ₂ OOCCH ₃		CH ₃	CH ₃	C ₄ H ₉ -n

5-SO ₂ N(CH ₃) ₂	OCH ₃	H	CH ₃	CH ₃	C ₂ H ₅
5-SO ₃ C ₆ H ₅	CH ₃	H	CH ₃	CH ₃	C ₂ H ₅
5-CN	H	H	H	H	CH ₃
5-CONH ₂	CH ₂ CH ₂ COOCH ₃	H	CH ₃	CH ₃	C ₆ H ₅
4-COOCH ₃	CH ₂ CH(OH)CH ₂ OH	H	CH ₃	CH ₃	C ₆ H ₁₁
6-COCH ₃	CF ₃	H	CH ₃	CH ₃	C ₂ H ₅
6-COC ₆ H ₅	CF ₃	H	CH ₃	CH ₂ SO ₃ K	CH ₂ CH ₂ OH
6-Cl	H	C ₂ H ₅	C ₂ H ₅	CH ₂ SO ₃ H	CH ₂ CH ₂ OH
5,6-di-Cl	H	C ₂ H ₅	C ₂ H ₅	CH ₃	CH ₂ CH ₂ OH
4-Br	CH ₂ CH(Cl)CH ₂ Cl	C ₂ H ₅	C ₂ H ₅	CH ₃	CH ₂ CH ₂ OC ₂ H ₅
4-CF ₃	CH ₂ CH(OCH ₃)CH ₂ OCH ₃	CH ₃	CH ₃	CH ₃	CH ₂ CN
5-NHCOCH ₃	CH ₃	CH ₃	CH ₃	CH ₃	CH ₂ CONH ₂
5-SO ₂ CH ₃	CH ₃	CH ₃	CH ₃	CH ₃	CH ₂ CONHCH ₃
5-CH ₂ SO ₂ NHC ₂ H ₅	CH ₃	CH ₃	CH ₃	CH ₃	CH ₂ CON(C ₂ H ₅) ₂
5-CH ₂ SO ₂ N(C ₂ H ₅) ₂	CH ₃	CH ₃	CH ₃	CH ₃	CH ₂ NHCOCH ₃
5-SO ₂ NHC ₂ H ₅	H	CH ₃	CH ₃	CH ₃	CH ₂ NHCOOCH ₃
5-CH ₂ CH ₂ NHCOCH ₂ Cl	H	CH ₃	CH ₃	CH ₃	CH ₂ OOCCH ₃

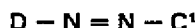
5-CH ₂ NHSO ₂ CH ₃	CH ₃	CH ₃	CH ₃	CH ₃	CH ₃	CH ₂ (C ₄ H ₆ ON)
5-CH ₂ CH ₂ CH ₂ (C ₄ H ₆ ON)	CH ₂ CH ₂ OH	CH ₃	CH ₃	H	CH ₃	CH ₂ CH ₂ COOCH ₃
None	CH ₂ Cl	CH ₃	CH ₃	H	H	CH ₂ CH ₂ COOCH ₃
5-CH ₂ CH ₂ CN	OCH ₂ Cl	CH ₃	CH ₃	C ₃ H ₇ -n	H	H
5-NHCOCH ₂ CN	OCH ₃	CH ₃	CH ₃	C ₃ H ₇ -n	C ₂ H ₅	C ₂ H ₅
5-CH ₂ (C ₄ H ₄ O ₂ N)	OCH ₃	CH ₃	CH ₃	C ₂ H ₅	C ₃ H ₇ -n	C ₃ H ₇ -n
5-CH ₂ (C ₅ H ₆ O ₂ N)	CH ₂ CH ₂ CN	CH ₃	CH ₃	C ₂ H ₅	C ₄ H ₉ -n	C ₄ H ₉ -n
5-CH ₂ CH ₂ (C ₈ H ₄ O ₂ N)	Cl	CH ₃	CH ₃	C ₂ H ₅	C ₂ H ₅	C ₂ H ₅
5-CH ₂ CONH ₂	Cl	CH ₃	CH ₃	CH ₃	C ₂ H ₅	C ₂ H ₅
6-CH ₂ CONHCH ₃	H	CH ₃	CH ₃	CH ₃	CH ₃	CH ₃
6-CH ₂ CH ₂ OCH ₂ CH ₂ OC ₂ H ₅	OCH ₃	CH ₃	CH ₃	CH ₃	C ₆ H ₅	C ₆ H ₅
5-COOCH ₂ CH ₂ OCH ₃	NHCHO	CH ₃	CH ₃	CH ₃	C ₆ H ₁₁	C ₆ H ₁₁
5-CH ₂ CH ₂ SCH ₃	NHCOCH ₂ OCCH ₃	CH ₃	CH ₃	CH ₃	C ₂ H ₅	C ₂ H ₅
5-CH ₂ CH ₂ CH ₂ Cl	NHCOCH ₂ CH ₃	H	H	H	CH ₂ CH ₂ OH	CH ₂ CH ₂ OH
5-CH ₂ SC ₆ H ₅	NHCOCH ₂ Cl	H	H	CH ₃	CH ₂ CH ₂ OH	CH ₂ CH ₂ OH
5-CH ₂ SO ₂ CH ₃	NHCOC ₆ H ₅	CH ₃	CH ₃	CH ₃	CH ₂ CH ₂ OH	CH ₂ CH ₂ OH
5-CH ₂ SO ₂ C ₆ H ₅	NHCOC ₂ H ₅	CH ₃	CH ₃	CH ₃	CH ₂ CH ₂ OC ₂ H ₅	CH ₂ CH ₂ OC ₂ H ₅

5-CH ₂ CH(OH)CH ₂ OH	NHCOC ₆ H ₁₁	H	CH(CH ₃) ₂	CH ₃	CH ₂ CN
6-CH ₂ CH(OH)CH=CH ₂	H	H	CH ₃	CH ₃	CH ₂ CONH ₂
4-C ₆ H ₄ -P-OH	CH ₂ SCH ₃	H	CH ₃	H	CH ₂ CONHCH ₃
5-C ₆ H ₄ -P-C ₂ H ₅	CH ₂ CH=CH ₂	H	CH ₃	H	CH ₂ CON(C ₂ H ₅) ₂
5-C ₆ H ₄ -P-OC ₆ H ₅	Br	H	CH ₃	H	CH ₂ NHCOCH ₃
5-C ₆ H ₄ -P-C ₆ H ₁₁	I	H	CH ₃	CH ₃	CH ₂ NHCOOCH ₃
5-C ₆ H ₄ -P-(C ₄ H ₃ O)	F	H	CH ₃	CH ₃	CH ₂ OOCCH ₃
5-C ₆ H ₄ -P-OCC ₆ H ₅	SCH ₃	H	CH ₃	CH ₃	CH ₂ (C ₄ H ₆ ON)
5-C ₆ H ₄ -O-COOCH ₃	CH ₂ OOCCH ₃	C ₂ H ₅	C ₂ H ₅	C ₂ H ₅	CH ₂ CH ₂ COCH ₃
5-C ₆ H ₄ -M-SO ₂ NH ₂	OCH ₃	CH ₃	CH ₃	CH ₃	CH ₂ CH ₂ COOCH ₃
5-C ₆ H ₄ -P-CONH ₂	CH ₃	CH ₃	CH ₃	CH ₃	H
5-C ₆ H ₄ -P-NHCONHCH ₃	H	C ₃ H ₇ -n	C ₃ H ₇ -n	H	C ₂ H ₅
5-C ₆ H ₄ -M-(C ₈ H ₄ O ₂ N)	CH ₂ CH ₂ COOCH ₃	CH ₃	CH ₃	H	C ₃ H ₇ -n
5-C ₆ H ₃ -O, P-di-CN	CH ₂ CH(OH)CH ₂ OH	CH ₃	CH ₃	H	C ₄ H ₉ -n
6-C ₆ H ₂ -O, M, P-tri-Cl	CF ₃	C ₄ H ₉ -n	C ₄ H ₉ -n	H	C ₂ H ₅
5-C ₆ H ₄ -P-OCH ₂ CH ₂ OCH ₃	CF ₃	CH ₃	CH ₃	H	C ₂ H ₅
6-C ₆ H ₄ -P-SC ₆ H ₅	H	CH ₃	CH ₃	H	CH ₃

5-C ₆ H ₄ -p-SO ₂ CH ₃	H	CH ₃	H	C ₆ H ₅
5-C ₆ H ₄ -p-SO ₂ C ₆ H ₅	CH ₂ CH(Cl)CH ₂ Cl	H	H	C ₆ H ₁₁
5-C ₆ H ₁₀ -p-Cl	CH ₂ CH(OCH ₃)CH ₂ OCH ₃	CH ₃	CH ₃	C ₂ H ₅
5-C ₆ H ₉ -o,p-di-OH	CH ₃	CH ₃	CH ₃	CH ₂ CH ₂ OH
5-C ₆ H ₁₀ -p-CH ₃	CH ₃	CH ₃	CH ₃	CH ₂ CH ₂ OH
5-C ₆ H ₁₀ -p-OC ₂ H ₅	CH ₃	CH ₃	CH ₃	CH ₂ CH ₂ OH
5-CH ₂ CH ₂ SO ₂ NHC ₆ H ₅	CH ₃	CH ₃	CH ₃	CH ₂ CH ₂ OC ₂ H ₅
5-C ₆ H ₄ -p-SO ₂ NHC ₆ H ₅	H	CH ₃	CH ₃	CH ₂ CN
5-CH ₂ CH ₂ OCH ₂ C ₆ H ₅	H	CH ₃	CH ₃	CH ₂ CONH ₂
5-SO ₃ K	H	CH ₃	CH ₃	C ₂ H ₅
5-SO ₃ NH(Et) ₃	H	CH ₃	CH ₃	CH ₂ CH ₂ OH
5,6-di-Cl	CH ₃	CH ₃	CH ₃	C ₂ H ₅
5,6-di-Cl	CH ₃	CH ₃	CH ₂ SO ₃ ⁻ Na ⁺	C ₂ H ₅

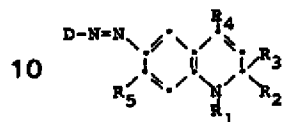
CLAIMS

1. A dye of the formula



wherein D is unsubstituted or substituted 2-benzothiazolyl or 3-benzisothiazolyl and C¹ is an unsubstituted or substituted 1,2-dihydroquinoline coupler.

2. A dye according to claim 1 wherein the coupler C' is of the formula

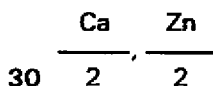


wherein R₁ is H or a group selected from alkyl, aryl and cyclohexyl, which groups are
15 unsubstituted or substituted with 1–3 substituents different from the said group and indepen- 15
dently selected from hydroxy, alkoxy, aryl, aryloxy, cyclohexyl, cyclohexoxy, furyl, aroyloxy,
alkoxycarbonyl, alkanoyloxy, SO₂NH₂, alkyl-SO₂M, SO₂NHaryl, SO₂NHalkyl, SO₂N-(alkyl)₂,
NHCOOalkyl, NHCONHalkyl, acylamido, alkylsulfonamido, succinimido, glutarimido, phthalim-
ido, 1-(2-pyrrolidono), cyano, CONH₂, CONHalkyl, CON(alkyl)₂, alkoxyalkoxy, alkylthio, halogen,
20 arylthio, alkylsulfonfyl and arylsulfonfyl; 20

R_2 and R_3 are each independently selected from H and alkyl;

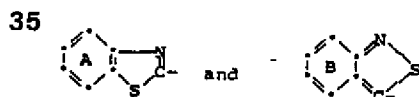
R_4 is H, alkyl, or alkyl-SO₂M; and

R₅ is selected from H, alkyl, alkoxy, alkenyl of 2-8 carbons, halogen, acylamido, alkyl-thio and formamido, wherein the alkyl moieties thereof are unsubstituted or substituted with 1-3 substituents independently selected from hydroxy, halogen, cyano, alkoxy, alkylthio, alkyl-SO₃M, alkanoyl, alkanoyloxy, and alkoxycarbonyl, wherein M is selected from H, Na, K, NH₄.



and the colorless cations of salts of primary, secondary and tertiary aliphatic and aryl amines.

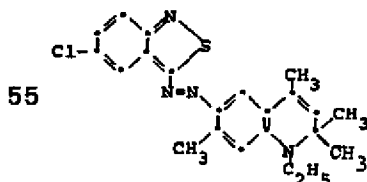
3. A dye of Claim 1 or 2 wherein D is selected from



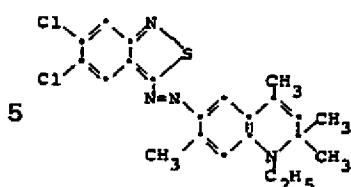
wherein rings A and B are unsubstituted or substituted with 1-3 substituents independently selected from alkyl, cyclohexyl, aryl, alkoxy, thiocyno, alkylthio, arylthio, cyano, CONH₂, CONHalkyl, CON(alkyl)₂, alkoxy carbonyl, -NO₂, alkanoyl, aroyl, alkanoyloxy, alkylsulfonyl, SO₂NH₂, SO₂NHalkyl, SO₂N(alkyl)₂, alkyl-SO₃M, alkylsulfonamido, acylamido, halogen, trifluoro-
45 methyl, SO₃-alkyl, SO₃-alkyl, and alkenyl of 2-8 carbons, and wherein all of the alkyl, cyclohexyl 45 and aryl moieties of the above groups are unsubstituted or substituted as for R₁.

4. A dye according to claim 3 wherein rings A and B are unsubstituted for substituted with 1-3 substituents independently selected from cyano, alkylsulfonyl, SO_2NH_2 , $-\text{NO}_2$, SO_2NHal , alkyl, alkyl- SO_2M , $\text{SO}_2\text{N(alkyl)}$, and halogen.

5. A dye of Claim 1 of the formula



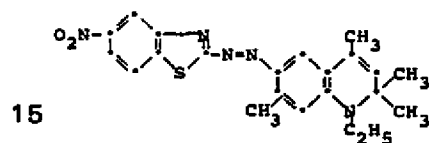
- 60 6. A dye of Claim 1 of the formula



7. A dye of Claim 1 of the formula

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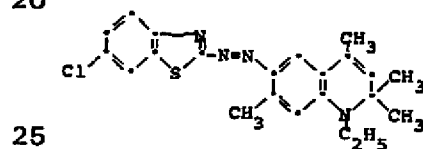


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8. A dye of Claim 1 of the formula

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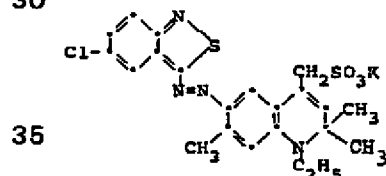


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9. A dye of Claim 1 of the formula

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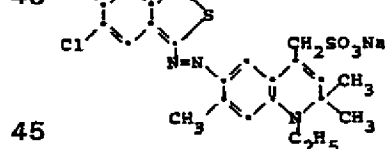


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10. A dye of Claim 1 of the formula

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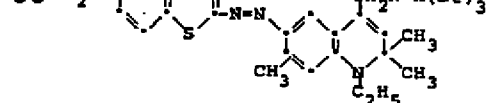


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11. A dye of Claim 1 of the formula

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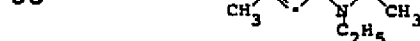
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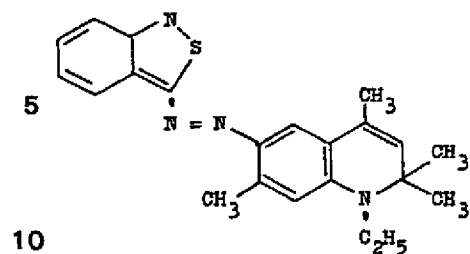
12. A dye of Claim 1 of the formula

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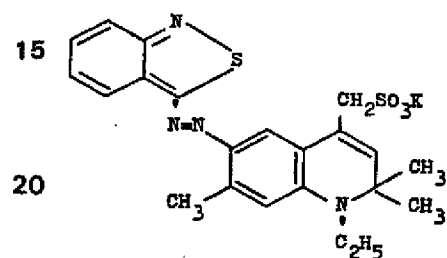
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13. A dye of Claim 1 of the formula



14. A dye of Claim 1 of the formula



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